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<b>(54) Title:</b> FROZEN FOOD PRODUCT  <b>(57) Abstract</b>  A frozen food product comprising AFPs, said product having an average ice crystal size of 0.01 to 20 micrometer, wherein said crystal size is maintained between 0.01 and 20 micrometer upon storage for 3 weeks at -10 °C. Additionally a process for the manufacture of the frozen food product comprising AFPs is described, wherein the process comprises one or more of the following steps: (i) a (pre-)freezing step which is a nucleation dominated freezing step; (ii) a (post-)compaction step using a screw extruder or a compactor.		

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Frozen Food productTechnical Field of the Invention

5 The invention relates to food products containing Anti-freeze peptides (AFPs), in particular to frozen food products containing AFPs.

Background to the Invention

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Anti-freeze peptides (AFPs) have been suggested for improving the freezing tolerance of foodstuffs. In particular it has been suggested that some AFPs may be capable of increasing the smooth texture of frozen food products such as ice cream. Up till now, however the use of AFPs has not been applied to commercially available food products. One reason for this is that up till now it has proved difficult to reproducibly produce a frozen food product having the desired texture and eating characteristics.

20

WO 90/13571 discloses antifreeze peptides produced chemically or by recombinant DNA techniques from plants. The AFPs can suitably be used in food products such as ice cream. No guidelines are given as to how to obtain smooth textures.

25

WO 92/22581 discloses AFPs from plants, which can be used for controlling ice crystal growth. This document also describes a process for extracting a polypeptide composition from intercellular spaces of plants by infiltrating leaves with an extraction medium without rupturing the plant cells.

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Applicants believe that one of the possible reasons for the lack of desired texture in frozen food products containing AFP is that although the AFP is capable of recrystallisation inhibition it is often not capable of avoiding less  
5 favourable hard and brittle textures. Applicants believe that one of the explanations for this is that AFPs seem capable of controlling the growth of the ice-crystals. However the presence of AFP may also lead to an adverse effect in that the ice crystals tend to form aggregates  
10 leading to hard and brittle products. Thus the texture of the product is unfavourably affected during the manufacturing process.

The present invention therefore aims at defining  
15 manufacturing conditions which improve the texture of AFP containing frozen food products.

Surprisingly it has now been found that if the conditions for producing the frozen food material are carefully chosen,  
20 this leads to an improved texture. In particular applicants have found that if the production process includes the use of one or more of the following steps;

(i) a (pre-)freezing step which is a nucleation dominated  
25 freezing process;

(ii) a (post-)compaction step using a screw extruder or a (piston) compactor;

30 this leads to aggregation of the ice crystals being minimised and therefore results in more favourable textures of the frozen product, said texture being maintained for prolonged storage periods.

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Generally in the freezing of a composition, two distinct phases can be seen: at the onset of the freezing process many small ice crystals are rapidly formed. This phase is called the nucleation phase of the freezing process. Following the nucleation process the remaining part of the composition freezes onto the surface of the nucleates and therewith contributes to the growth of the ice crystals. This phase in the freezing process is called the growth phase. In a growth dominated freezing process most of the composition is frozen during the growth phase, in a nucleation dominated freezing process most of the composition is frozen during the nucleation phase.

Traditional freezing processes for frozen confectionery products for example involves the use of scraped surface heat exchangers whereby the mix to be frozen is subjected to shear during the freezing process. Generally this freezing process takes from 5 to 30 minutes for the product to reach a temperature of  $-5^{\circ}\text{C}$  or lower. In this process initially some nucleation of ice crystals occurs followed by a period wherein ice crystal growth dominates.

Alternative freezing processes, which for example are used for the freezing of water ice involves the low shear or quiescent freezing of the mix, for example by filling a mould and dipping the mould into a cold bath, for example filled with brine. In this process initial nucleation of ice crystals takes place at the surface of the mould, the internal of the product then tend to freeze more slowly in a freezing process dominated by growth.

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Applicants have now surprisingly found that the aggregation in AFP containing products can significantly be reduced if a nucleation dominated freezing process is chosen. Such a freezing process is generally characterised by a short  
5 freezing time in combination with the formation of small ice crystals. Preferably the freezing process is carried out under low shear or quiescent freezing conditions.

10 Disclosure of the Invention

Accordingly, in a first aspect the present invention relates to a process for the manufacture of a frozen food product comprising AFPs, wherein the process comprises one or more  
15 of the following steps;

(i) a (pre-)freezing step which is a nucleation dominated freezing process;

20 (ii) a (post-)compaction step using a screw extruder or a (piston) compactor;

For the purpose of this invention the term AFP has the meaning well-known in the art, see for example "Antifreeze  
25 proteins and their potential use in frozen food products", Marilyn Griffith and K. Vanya Ewart, Biotechnology Advances, Vol 13, pp 375-402, 1995.

The present invention aims at providing the food  
30 manufacturer with a greater flexibility for using AFP material in frozen food products when aiming to obtain a product with improved recrystallisation properties in combination with a good texture. In particular it has been

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found that the texture of frozen food products containing AFPs can markedly be improved by carefully controlling its production method.

5 The invention is based on the finding that if the frozen product is produced by a process involving one or more of the following process steps;

(i) a (pre-)freezing step which is a nucleation dominated  
10 freezing process;

(ii) a (post-)compaction step using a screw extruder or a (piston) compactor;

15 this can lead to an improved texture of the product.

Applicants believe that it is well within the ability of the skilled person to select those freezing methods which result in a nucleation dominated freezing processes.

20

Preferably when the freezing process is a nucleation dominated freezing process, the freezing process is such that the product reaches a temperature of  $-5^{\circ}\text{C}$  or lower within 30 seconds, preferably in 0.01 to 25 seconds, most  
25 preferably in 1 to 15 seconds.

Also preferably when the freezing process is a nucleated dominated freezing process, the freezing process is such that it results in many relatively small crystals, whereby  
30 the average size of the crystals is from 0.01 to 20 micrometer, more preferred from 0.01 to 15 micrometer most preferred from 0.01 to 10 micrometer.

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For example rapid freezing processes tend to be nucleation dominated. Suitable processes may for example involve:

- 5 (a) surface freezing, preferably film freezing onto a cold surface;
- (b) freezing of supercooled systems;
- (c) decompression freezing;
- (d) freezing by very low temperatures;
- 10 (e) rapid particulate freezing, preferably condensation freezing.

Other rapid freezing processes will be apparent to the skilled person and are also embraced in the scope of the present invention. Preferably the freezing processes involve  
15 no or low shear.

Surface freezing preferably involves the application of a thin film or discrete particles onto a cold surface, optionally followed by removal of the frozen material.  
20 Preferably the film or particle thickness is from 0.01 to 5 mm. The cold surface is preferably at a temperature below -15°C, more preferred less than -20°C, most preferred less than -25°C. Suitably the surface can be cooled by applying liquid nitrogen, glycols or methanol. The removal can be  
25 done by any suitable means, for example by scraping, therewith producing frozen particles, for example flakes or pellets which can then be further processed. Obviously during further processing care should be taken to avoid substantial melting of the composition, which may result in  
30 growth dominated re-freezing.

In a very preferred embodiment surface freezing involves film freezing on a drum freezer which is for example cooled



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with liquid nitrogen or methanol, followed by removal of the film from the drum freezer.

5 In a further embodiment of surface freezing a cryogenic plate freezer cooled with liquid nitrogen is used to produce frozen pellets.

10 An alternative form of surface freezing involves the preparation of a cold core followed by applying the mix to be frozen to the core for example by dipping or spraying, whereby a relatively thin film adheres to the cold core. Advantageously, such a cold core may for example be a very cold (e.g. dipped into liquid nitrogen) ice-cream core where upon a thin film of water-ice comprising AFP is frozen.

15 Another method of achieving rapid, nucleation dominated freezing is to produce a supercooled system at low temperatures followed by sudden freezing e.g. by applying a shock to the supercooled liquid. The rapid freezing of a  
20 supercooled liquid generally is a nucleation dominated freezing process.

Preferably the supercooled liquid has a temperature of at least 1 degree below the melting point, more preferred from  
25 1-20 degrees below the melting point, for example 2-10 degrees below the melting point.

A third method of achieving rapid nucleation dominated freezing is to use decompression freezing. This involves the  
30 applying of high pressures to a liquid system while cooling it followed by removing the overpressure. This removal of the pressure then results in a rapid nucleation dominated freezing.

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Preferably the pressure to be applied is from 100 to 3000 bar, for example from 200 to 2000, generally from 300 to 1300 bar. The temperature of the product before removing the  
5 over-pressure is preferably at least 5 degrees below the melting point at atmospheric pressure, preferably 6-10 degrees below the melting point.

A fourth method of ensuring nucleation dominated freezing is  
10 the application of very low temperatures. For example small drops of material to be frozen may be immersed into a fluid freezing medium e.g. liquid hexane or liquid nitrogen. Preferably the freezing temperature for this method is less than -50 °C. This method works best for relatively small or  
15 thin products to be frozen. Small products are preferably less than 5 grams, more preferred from 0.001 to 3 grams, most preferred 0.01 to 1 gram and may for example be drops of liquid immersed in the freezing medium. Relatively thin products may for example be sheets or thin streams of  
20 products, preferably having at least 1 dimension of less than 2 cm, more preferred 0.1 to 0.5 cm.

The product for use in this method may for example be directly immersed into the freezing liquid, alternatively  
25 however the products are first contacted with a protective layer e.g. filled into a mould, pumped through a pipe whereby these are contacted with the cooling medium.

A fifth preferred method to freeze food products of the  
30 invention involves rapid particulate freezing, preferably condensation freezing. This may for example be achieved by spraying a liquid mix to be frozen into a very cold gaseous environment or into a cooled environment. An especially

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preferred method for rapidly freezing a liquid into particulates is condensation freezing. Most preferred is the use of techniques which are for example use in the production of artificial snow.

5

The production of artificial snow is widely described in the literature. Often artificial snow is produced in so called snow cannons whereby the water is frozen by spraying a mixture of water and pressurised air. Preferably the snowmaking takes place in an environment having a temperature of less than  $-3^{\circ}\text{C}$ , most preferred  $-5$  to  $-50^{\circ}\text{C}$  and a relative humidity of less than 75%, most preferred less than 50%.

15 Frozen particulates obtained by this fifth method can vary in size, but generally the number average diameter of the particles will be up to 10 mm, more preferred less than 5 mm. Generally each particulates will comprise multiple aggregated ice-crystals.

20

The freezing of frozen confectionery products by means of a screw extruder is for example described in: EP 713,650 (Societe des Produits Nestle), EP 410,512 (HMF Krampe & Co et al); EP 561,118 (Milchhof-Eiskrem GmbH et al),  
25 EP 351,476 (Goavec S.A. Societe Dite).

Preferably the manufacturing process of the invention involves the use of a screw extruder whereby the extrusion temperature of the frozen product is  $-8^{\circ}\text{C}$  or lower, more  
30 preferred from  $-10$  to  $-25^{\circ}\text{C}$ , most preferred from  $-12$  to  $-20^{\circ}\text{C}$ .

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Suitable screw extruders for use in the process of the invention can for example be twin screw extruders such as described for example in EP 561,118. Also single screw extruders may be used. Also extruders may be used which  
5 combine more than one function of the ice-cream manufacturing process (see for example EP 713,650).

The conditions under which the screw extruder operates may vary for example depending on the type and size of the  
10 extruder used. Applicants believe that it is well within the ability of the skilled person to select those operating conditions such that a favourable quality of the product is obtained. Examples of suitable operating conditions are given in the examples.

15 Alternatively a compactor may advantageously be used in the manufacturing of frozen food products with AFPs. All suitable compactors such as presses may be used, especially preferred is the use of a piston compactors whereby pressure  
20 is applied onto the food products by means of the movement of a piston. Traditionally piston compactors have for example been used in the filling of sausages. Again applicants believe that it is within the ability of the skilled person to select the appropriate operating  
25 conditions of the (piston) compactor.

Preferably the invention relates to a process for the manufacture of a frozen food product comprising AFPs, wherein the process comprises the following steps;  
30

(i) a (pre-)freezing step which is a nucleation dominated freezing process; and

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(ii) a (post-)compaction step using a screw extruder or a (piston) compactor.

The use of a screw extruder or compactor may very  
5 advantageously applied to products which have been pre-frozen under such conditions that a particulate (partial) frozen material is produced for example flakes, pellets, powders, extended rods or sheets. For these pre-frozen products the use of screw extruders or (piston) compactors  
10 may advantageously lead to the compaction of the particulate material into a more solid structure.

The complete manufacturing process of the frozen products of the invention may comprise further optional steps in  
15 addition to pre-freezing and/or screw extrusion or piston compaction. For example the mixing of the ingredients, ageing, pasteurisation, homogenisation, pre-aeration etc. These optional steps can take place in any suitable order.

20 As described above, one of the characteristics of nucleation dominated freezing process is the formation of many small ice crystals. Applicants have found that the combined use of AFPs as an ingredient and nucleation dominated freezing process leads to a particular advantageous texture of the  
25 products to be frozen, said textures being maintained for long storage periods.

Particularly the nucleation dominated freezing process can very advantageously be used for the production of a  
30 particulate frozen material. Examples of these are frozen flakes, frozen (small) droplets, frozen powders, pellets, frozen rods and frozen snow. Surprisingly particulate materials formed by the process of the invention have a

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reduced tendency to aggregation and therefore the free flowing nature of the particulate material can be maintained over storage, even if the storage temperature is relatively high.

5

Further the applicants have found that the use of a screw extruder or (piston) compactor in the production of AFP containing frozen food products is very advantageous in that it too can lead to very small ice-crystal sizes which can be maintained for long periods of storage.

10

Preferably the freezing conditions are chosen such that the average size of the ice crystals in the final frozen product is from 0.01 to 20 micrometer, said ice crystal sizes to be maintained in said range upon storage at -10 °C for 3 weeks.

15

Preferably the average ice crystal size remains less than 15 micrometer, for example less than 12 or even 10 micrometer during storage for 3 weeks at -10°C.

20

If the freezing process involves a nucleation dominated freezing process in the absence of any compaction process, the frozen product provided may be a particulate food product. If, on the other hand, a screw extruder or a (piston) compactor is used, products may be formed which are homogeneously solid and having no (fine) particulates.

25

Preferably non-particulate products of the invention have a smallest dimension of more than 2 cm, more preferred more than 2.5 cm, most preferred more than 3 cm.

30

After freezing the product may be further handled. For example the product may be filled into packages say of 0.05

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to 10 litres and then stored. Alternatively the product may be further shaped or formed into the final product. For example the product can be used to the shaped into ice-cream gateaux.

5

A further advantage of the invention is that when the process used includes post compaction using either a screw extruder or a (piston) compactor, products of the invention generally do not need to be subjected to a hardening step, for example in a hardening tunnel. This advantage has for example been suggested for AFP products in general in US 5,620.732 (Pillsbury).

The process as described in US 5,620,732 however has as a disadvantage that this is not suitable for the production of luxury stick products. These products are traditionally made by extruding and cutting a block of ice-cream, hardening the block, followed by stick insertion and coating for example with chocolate or fruit water ice. If the hardening step is omitted for AFP containing products this leads to problems in the further handling for example during stick insertion or further coating.

Surprisingly applicants have found that the combined use of AFPs and post-compaction with either a screw extruder or (piston) compactor now renders it possible to product luxury stick products without the use of a hardening step.

Frozen food products of the invention may be any food product which can be stored and/or eaten in the frozen state. Examples of frozen food products which may contain AFPs are processed food products such as for example frozen bakery products for example dough, batters, cakes etc.,

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frozen culinary products for example soups, sauces, pizzas, frozen vegetable products such a compote, mashed potato, tomato paste etc.

- 5 Applicants have found that the method of the invention is best applicable to food systems which are fluid or liquid prior to freezing. A very preferred food product according to the invention is a frozen confectionery product.
- 10 For the purpose of the invention the term frozen confectionery product includes milk containing frozen confections such as ice-cream, frozen yoghurt, sherbet, ice milk and frozen custard; as well as frozen confections which do not typically contain milk such as water ices, sorbet,
- 15 granitas and frozen fruit purees. Especially preferred products of the invention are ice-cream and water ice.

Frozen products according to the invention may be aerated. For example the level of aeration is more than 50%, more

20 preferably more than 70%, most preferable more than 90%. Generally the level of aeration will be less than 400%, more general less than 300%, most preferred less than 200%. Aeration may for example take place prior or during freezing. If the product is pre-frozen by one or more of the

25 above described nucleation dominated freezing processes then preferably the aeration takes place prior to pre-freezing.

Preferably the level of AFPs in the frozen food product of the invention is from 0.0001 to 0.5 wt% based on the final

30 product.

The AFP for use in products of the invention can be any AFP suitable for use in food products. Examples of suitable



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sources of AFP are for example given in the above mentioned article of Griffith and Vanya Ewart and in patent applications WO 98/04699, WO 98/04146, WO 98/04147, WO 98/04148 and WO 98/22591.

5

The AFPs can be obtained from their sources by any suitable process, for example the isolation processes as described in the above mentioned documents.

- 10 One possible source of AFP materials is fish. Examples of fish AFP materials are AFGP (for example obtainable from Atlantic cod, Greenland cod and Tomcod), Type I AFP (for example obtainable from Winter flounder, Yellowtail flounder, Shorthorn sculpin and Grubby sculpin), Type II AFP  
15 (for example obtainable from Sea raven, Smelt and Atlantic herring) and Type III AFP (for example obtainable from Ocean Pout, Atlantic wolffish, Radiated shanny, Rock gunnel and Laval's eelpout). A preferred example of the latter type is described in WO 97/02343.

20

Another possible source of AFP material are invertebrates. Also AFPs may be obtained from Bacteria.

- A third possible source of AFP material are plants. Examples  
25 of plants containing AFPs are garlic-mustard, blue wood aster, spring oat, winter cress, winter canola, Brussels sprout, carrot, Dutchman's breeches, spurge, daylily, winter barley, Virginia waterleaf, narrow-leaved plantain, plantain, speargrass, Kentucky bluegrass, Eastern  
30 cottonwood, white oak, winter rye, bittersweet nightshade, potato, chickweed, dandelion, spring and winter wheat, triticale, periwinkle, violet and grass.

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Both natural occurring species may be used or species which have been obtained through genetic modification. For example micro-organisms or plants may be genetically modified to express AFPs and the AFPs may then be used in accordance to  
5 the present invention.

Genetic manipulation techniques may be used to produce AFPs. Genetic manipulation techniques may be used to produce AFPs having at least 80%, more preferred more than 95%, most  
10 preferred 100% homology to the AFPs directly obtained from the natural sources. For the purpose of the invention these AFPs possessing this high level of homology are also embraced within the term "AFPs".

15 The genetic manipulation techniques may be used as follows: An appropriate host cell or organism would be transformed by a gene construct that contains the desired polypeptide. The nucleotide sequence coding for the polypeptide can be inserted into a suitable expression vector encoding the  
20 necessary elements for transcription and translation and in such a manner that they will be expressed under appropriate conditions (for example in proper orientation and correct reading frame and with appropriate targeting and expression sequences). The methods required to construct these  
25 expression vectors are well known to those skilled in the art.

A number of expression systems may be utilised to express the polypeptide coding sequence. These include, but are not  
30 limited to, bacteria, yeast insect cell systems, plant cell culture systems and plants all transformed with the appropriate expression vectors.

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A wide variety of plants and plant cell systems can be transformed with the nucleic acid constructs of the desired polypeptides. Preferred embodiments would include, but are not limited to, maize, tomato, tobacco, carrots,  
5 strawberries, rape seed and sugar beet.

For the purpose of the invention preferred AFPs are derived from fish or plants. Especially preferred is the use of fish proteins of the type III, most preferred HPLC 12 as  
10 described in our case WO 97/02343. From plants especially the use of AFPs from carrot or grass are preferred.

For some natural sources the AFPs may consist of a mixture of two or more different AFPs.

15

Preferably those AFPs are chosen which have significant ice-recrystallisation inhibition properties. This can be measured in accordance to Example I.

20 Preferably AFPs in accordance to the invention provide an ice particle size upon recrystallisation, as measured in accordance to the examples, of less than 20  $\mu\text{m}$ , more preferred from 5 to 15  $\mu\text{m}$ .

25 Preferably the level of solids in the frozen food product (for example sugar, fat, flavouring etc.) is more than 2 wt%, more preferred from 4 to 70wt%.

The method of preparing the frozen food product of the  
30 invention can be selected from any suitable method for the preparation of frozen food products. The AFPs can generally be added at various stages of the preparation, for example it can be added in the first pre-mix of ingredients or can

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later be added during a later stage of the preparation process. For some applications it is sometimes preferred to add the AFPs at a relatively late stage of the production process, for example after (partial) pre-freezing of the product.

The freezing process of the invention will generally include the freezing of the composition say to a temperature of less than  $-2^{\circ}\text{C}$ , say from  $-80$  to  $-5^{\circ}\text{C}$ . If desired, products of the invention do not need to be subjected to low temperatures to avoid ice-crystal growth. Therefore the products may for example be frozen without the need to use low temperatures say less than  $-25^{\circ}\text{C}$  and can also be stored at temperatures which are higher than traditional temperatures to store frozen confectionery products.

Preferably the freezing process involves conditions of low or no shear e.g. found in the freezing of filled moulds , dipping, thin film crystallisation, dropping into liquid nitrogen etc.

For some applications it may be advantageous to include a mixture of two or more different AFPs into the food product. One reason for this can for example be that the plant source for the AFPs to be used, contains more than one AFP and it is more convenient to add these, for example because they are both present in the AFP source to be used. Alternatively it may sometimes be desirable to add more than one AFP from different sources.

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The invention will now be illustrated by means of the following examples.

**Example I**

5

Method of determining whether an AFP possesses ice recrystallisation inhibition properties.

Recrystallisation inhibition properties can be measured using a modified "splat assay" (Knight et al, 1988). 2.5 µl of the solution under investigation in 30% (w/w) sucrose is transferred onto a clean, appropriately labelled, 16 mm circular coverslip. A second coverslip is placed on top of the drop of solution and the sandwich pressed together between finger and thumb. The sandwich is dropped into a bath of hexane held at -80°C in a box of dry ice. When all sandwiches have been prepared, sandwiches are transferred from the -80°C hexane bath to the viewing chamber containing hexane held at -6°C using forceps pre-cooled in the dry ice. Upon transfer to -6°C, sandwiches can be seen to change from a transparent to an opaque appearance. Images are recorded by video camera and grabbed into an image analysis system (LUCIA, Nikon) using a 20x objective. Images of each splat are recorded at time = 0 and again after 60 minutes. The size of the ice-crystals in both assays is compared by placing the slides within a temperature controlled cryostat cabinet (Bright Instrument Co Ltd, Huntington, UK). Images of the samples are transferred to a Quantimet 520 MC image analysis system (Leica, Cambridge UK) by means of a Sony monochrome CCD videocamera. Ice crystal sizing was performed by hand-drawing around ice-crystal. At least 400 crystals were sized for each sample. The ice crystal size was taken as being the longest dimension of the 2D projection of each

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crystal. The average crystal size was determined as the number average of the individual crystal sizes. If the size at 30-60 minutes is similar or only moderately (less than 10%) increased compared to the size at  $t=0$ , and/or the  
5 crystal size is less than 20 micrometer, preferably from 5 to 15 micrometer this is an indication of good ice-crystal recrystallisation properties

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**Example II**

The following formulation:

- 15%wt sugar
- 5 10%wt skimmed milk powder
- 10%wt butterfat
- 0.2%wt locust bean gum
- 0.2%wt monoglyceride
- 0.01%wt AFP\*
- 10 balance water

\* AFP HPLC 12 as described in WO 97/02343

- was produced using conventional ice-cream processing
- 15 equipment. The premix was cooled to 0°C
- before passing through a Megatron model MT1-63/3A mixer,
- operating at 8000 rpm. The mixer had a gap of 0.5mm between
- the rotor and stator. An equal volume of air was injected
- into the premix immediately before the mixing device. This
- 20 gave an overrun of 90% in the premix.

- This aerated premix was frozen by applying a 0.5mm thickness
- on a Gerstenberg and Agger pilot cooling drum, having a
- surface area of 0.2m<sup>2</sup>, and operating at a rotational speed of
- 25 5 rpm. The drum was cooled with liquid Nitrogen. Frozen
- flakes were removed using a plastic scraping knife after 1
- revolution (i.e. after 12 seconds). The flakes had a
- temperature of -20 °C. The flakes were collected, hardened in
- a blast freezer at -35 °C, then stored at -25 °C.

30

The ice-cream flakes were soft and creamy.

- 22 -

The particle size of the ice crystals were determined as in Example I. The ice crystal size was well below 20 micron and remained below 20 micron after storage for 3 weeks at  $-10^{\circ}\text{C}$ .



- 23 -

**Example III**

An ice-cream premix of the formulation of Example II was produced using conventional ice-cream processing equipment.

5 The premix was cooled to 0 °C before passing through a Megatron model MT1-63/3A mixer, operating at 8000 rpm and with a gap of 0.5mm between the rotor and stator. An equal volume of air was injected into the premix immediately before the mixing device. This gave an overrun of 90% in the  
10 premix.

The aerated premix was pumped through a plate heat exchanger, whose coolant temperature was controlled to -7 °C, a temperature warmer than the metastable limit of -8 °C for  
15 the premix. The premix exited the heat exchanger at -6 °C; the melting temperature of the premix was -2 °C. No ice was present in the premix, i.e. it was undercooled.

The premix was poured into conventional metal ice-lolly  
20 moulds, which were cooled by brine at -35 °C. Sticks were inserted into the moulds. After 15 minutes, the frozen ice-cream products were removed from the moulds.

The products were stored at -25 °C. The ice-cream products  
25 had a soft and creamy texture.

- 24 -

**Comparative Example IV**

An ice-cream premix of formulation of Example II was produced using conventional ice-cream processing equipment.

5 The premix was cooled to 0 °C before passing through a Megatron model MT1-63/3A mixer, operating at 8000 rpm and with a gap of 0.5mm between the rotor and stator. An equal volume of air was injected into the premix immediately before the mixing device. This gave an overrun of 90% in the  
10 premix.

The aerated premix was frozen in a standard ice-cream scraped surface heat exchanger (Crepaco W104, supplied by APV, operating with a series 80 dasher at a rotational speed  
15 of 240 rpm) at a rate of 200 l/hr. The exit temperature was -5 °C, after a residence time of 90 seconds. The ice-cream was then hardened in a blast freezer at -35 °C, before storage at -25 °C.

20 The ice-cream was found to be hard and brittle.

- 25 -

**Example V**

A liquid premix for the preparation of ice-cream was  
5 prepared by mixing:

	<b>Ingredient</b>	<b>% by weight</b>
	Skimmed milk powder	10.00
	sucrose	13.00
10	maltodextrin (MD40)	4.00
	Locust bean gum	0.14
	butter oil	8.00
	monoglyceride (palmitate)	0.30
	vanillin	0.01
15	AFP**	0.01
	water	balance

\*\* AFP is carrot AFP prepared as follows (WO 98/2259).  
Carrots (Daucus carota cv Autumn King) were grown in  
20 individual pots. When plants were approximately twelve weeks  
old, they were transferred to a cold room and held at 4°C in  
constant light during 4 weeks for cold-acclimation. Plants  
were watered three times a week. Root extract from cold  
acclimatised carrot roots was prepared by scrubbing freshly  
25 pulled cold acclimatised (as described above) carrots in cold  
water. The tops were removed and the juice extracted  
employing a domestic juice extractor (Russell Hobbs, model no  
9915). The juice was frozen in 1 litre blocks and stored at  
-20°C prior to collection for use in ice cream formulations.

30

The composition was prefrozen to -5 °C and aerated to 100%  
overrun in a traditional scraped surface heat exchanger.

- 26 -

The composition was further frozen in a single screw extruder having a barrel length of 0.75 m, a diameter of 0.2 m a screw pitch of 0.135 m (2 start) and a screw channel depth of 15 mm.

5

The throughput was 280 kg/hour, the inlet pressure 7 barg and a constant torque of the screw was 1500Nm. The output pressure was 8 barg. The screw extruder was cooled such that the extrusion temperature was -12 °C

10

As a comparison (B) the same product was produced using a conventional scraped surface heat exchanger.

15 A comparison (C) the same product was produced by the above screw extruder process, whereby the AFP was omitted from the formulation.

The resulting products were stored for 3 weeks at -10 °C.

20

Composition A had a smoother and creamier texture than formulations B and C.

- 27 -

**Example VI**

A liquid premix for the preparation of ice-cream was prepared by mixing:

5

Ingredient	% by weight
Skimmed milk powder	10.00
sucrose	13.00
maltodextrin (MD40)	4.00
10 Locust bean gum	0.14
butter oil	8.00
monoglyceride (palmitate)	0.30
vanillin	0.01
AFP (of example V)	0.01
15 water	balance

The liquid mix was continuously aerated at a throughput of 60 litres/hour using a high speed rotor/stator mixer (megatron, Kinematica AG) to an overrun of 100%. the mix  
20 temperature was 5 °C and a mixer speed of 1600 rpm was employed. A pressure of 3 barg was maintained within the mixing head.

The aerated mix was then continuously spread as a 0.1 mm  
25 film on the surface of a drum freezer cooled with a methanol solution at -28 °C. The drum freezer was rotated at a rate of 1rpm. After one complete revolution the frozen film at -10 °C was removed continuously by means of a scraper blade to form frozen flakes.

30

The frozen flakes were compressed batch-wise using a piston compression device. The compressed ice cream was extruded

- 28 -

through a nozzle and packaged for storage. The ice crystal size distribution of the frozen material was measured as follows: by placing the coverplates smeared with the compositions to be tested within a temperature controlled cryostat cabinet (Bright Instrument Co Ltd, Huntington, UK). Images of the samples are transferred to a Quantimet 520 MC image analysis system (Leica, Cambridge UK) by means of a Sony monochrome CCD videocamera. Ice crystal sizing was performed by hand-drawing around ice-crystal. At least 400 crystals were sized for each sample. The ice crystal size was taken as being the longest dimension of the 2D projection of each crystal. The average crystal size was determined as the number average of the individual crystal sizes.

15

The average ice crystal size was 5.8 micrometer for the fresh sample with AFP and 7.2 micrometer for the fresh sample with AFP. After storage for 3 weeks at -10 °C the particle size of the sample with AFP was 7.7. micrometer, without AFP 43.2 micrometer.

20

**Example VII**

5 Example VI was repeated, but now the pre-frozen flakes are fed via an hopper to a twin screw extruder (CP1050, APV) which was cooled with a methanol solution at -28 °C. Co-rotating fully intermeshing screw rotors were fitted and a rotational speed of 10 rpm was used. The ice-cream was compressed and extruded at a temperature of -12 °C.

- 30 -

**Example VIII**

A liquid premix for the preparation of ice-cream was prepared by mixing:

5

		<b>Ingredient</b>	<b>% by weight</b>
		Skimmed milk powder	10.00
		sucrose	13.00
		maltodextrin (MD40)	4.00
10		Locust bean gum	0.14
		butter oil	12.00
		monoglyceride (palmitate)	0.30
		vanillin	0.01
		AFP*	0.01
15		water	balance

\* AFP is AFP of HPLC-12 as described in WO 97/02343.

20 The mix was aerated to 100% overrun as in example VI. The aerated mix was frozen in the form of 10 mm diameter pellets using a cryogenic freezing unit (British Oxygen Company). The freezing surface consisted of a rotating horizontal turntable, which was cooled using liquid nitrogen to a temperature of -100 °C. The air above the freezing turntable  
25 was also cooled to a temperature of -120 °C, The turntable was rotated at 5rpm. After a single rotation the frozen pellets were swept off the freezing surface and collected.

30 The frozen pellets were then fed into a screw extruder under the same conditions as in Example VII.



# INTERNATIONAL SEARCH REPORT

International Application No

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## A. CLASSIFICATION OF SUBJECT MATTER

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## B. FIELDS SEARCHED

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IPC 6 A23G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 676 985 A (WU YALING ET AL) 14 October 1997	7-10
A	see column 6, line 18-23; claim 1	1-6
A	US 5 620 732 A (CLEMMINGS JOHN F ET AL) 15 April 1997 cited in the application see claims 1-4; examples 1,2	1-14
P, A	WO 98 04699 A (UNILEVER PLC ; UNILEVER NV (NL)) 5 February 1998 cited in the application see examples 3,4	1-14
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Date of the actual completion of the international search

9 June 1999

Date of mailing of the international search report

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# INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 561 118 A (MILCHHOF EISKREM GMBH &amp; CO            KG ;DEUTSCHES INST LEBENSMITTELTEC (DE))            22 September 1993            cited in the application            see claim 1</p>	7-14

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Information on patent family members

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5676985	A	14-10-1997	AT 179868 T	15-05-1999
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			WO 9611586 A	25-04-1996
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			AT 158151 T	15-10-1997
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>A23G 9/02</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/37164</b> <b>(43) International Publication Date:</b> 29 July 1999 (29.07.99)
<b>(21) International Application Number:</b> PCT/EP98/08552 <b>(22) International Filing Date:</b> 23 December 1998 (23.12.98) <b>(30) Priority Data:</b> 9801410.3 22 January 1998 (22.01.98) GB <b>(71) Applicant (for all designated States except AU BB CA GB IE IL KE LK LS MN MW NZ SD SG SZ TT UG US):</b> UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL). <b>(71) Applicant (for AU BB CA GB IE IL KE LK LS MN MW NZ SD SG SZ TT UG only):</b> UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> CHENEY, Paul, Edward [GB/GB]; Unilever Research Colworth, Colworth House, Sharnbrook, Bedford MK44 1LQ (GB). RUSSELL, Andrew [GB/NZ]; Chemical Engineering, Auckland University, Private Bag 92019, Auckland (NZ). <b>(74) Agent:</b> JOPPE, Hermina, L., P.; Unilever N.V., Patent Division, P.O. Box 137, NL-3130 AC Vlaardingen (NL).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> FROZEN FOOD PRODUCT  <b>(57) Abstract</b>  A frozen food product comprising AFPs, said product having an average ice crystal size of 0.01 to 20 micrometer, wherein said crystal size is maintained between 0.01 and 20 micrometer upon storage for 3 weeks at -10 °C. Additionally a process for the manufacture of the frozen food product comprising AFPs is described, wherein the process comprises one or more of the following steps: (i) a (pre-)freezing step which is a nucleation dominated freezing step; (ii) a (post-)compaction step using a screw extruder or a compactor.		

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		US 5345781 A	13-09-1994
		AT 158151 T	15-10-1997
		DK 561118 T	05-01-1993



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NOTIFICATION OF THE RECORDING  
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Unilever N.V.  
Patent Division  
P.O. Box 137  
NL-3130 AC Vlaardingen  
PAYS-BAS

Date of mailing (day/month/year) 29 June 2000 (29.06.00)	<b>IMPORTANT NOTIFICATION</b>
Applicant's or agent's file reference F 7414 (V)	
International application No. PCT/EP98/08552	International filing date (day/month/year) 23 December 1998 (23.12.98)

1. The following indications appeared on record concerning:

☐ the applicant ☐ the inventor ☒ the agent ☐ the common representative

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International application No. PCT/EP98/08552	

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State of Nationality

State of Residence

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From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents  
United States Patent and Trademark  
Office  
Box PCT  
Washington, D.C. 20231  
ÉTATS-UNIS D'AMÉRIQUE

in its capacity as elected Office

Date of mailing (day/month/year)

24 September 1999 (24.09.99)

International application No.

PCT/EP98/08552

Applicant's or agent's file reference

F 7414 (V)

International filing date (day/month/year)

23 December 1998 (23.12.98)

Priority date (day/month/year)

22 January 1998 (22.01.98)

Applicant

CHENEY, Paul, Edward et al

1. The designated Office is hereby notified of its election made:



in the demand filed with the International Preliminary Examining Authority on:

12 August 1999 (12.08.99)



in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

Dorothee Mülhausen

Telephone No.: (41-22) 338.83.38

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

17



Applicant's or agent's file reference F7414(C)/pmk	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/EP98/08552	International filing date (day/month/year) 23/12/1998	Priority date (day/month/year) 22/01/1998
International Patent Classification (IPC) or national classification and IPC A23G9/02		
Applicant UNILEVER PLC et al.		

- This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
- This REPORT consists of a total of 6 sheets, including this cover sheet.
  - ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 4 sheets.

- This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☒ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand  12/08/1999	Date of completion of this report  12. 05. 00
Name and mailing address of the international preliminary examining authority:   European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer  Krajewski, D  Telephone No. +49 89 2399 8472 

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/EP98/08552

**I. Basis of the report**

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

**Description, pages:**

1-30 as originally filed

**Claims, No.:**

1-17 with telefax of 24/01/2000

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:  
☐ the claims, Nos.:  
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

**IV. Lack of unity of invention**

1. In response to the invitation to restrict or pay additional fees the applicant has:

- ☐ restricted the claims.  
☐ paid additional fees.  
☐ paid additional fees under protest.  
☐ neither restricted nor paid additional fees.

2. ☒ This Authority found that the requirement of unity of invention is not complied and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/EP98/08552

3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is

☐ complied with.

☒ not complied with for the following reasons:

**see separate sheet**

4. Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this report:

☒ all parts.

☐ the parts relating to claims Nos. .

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

**1. Statement**

Novelty (N)	Yes:	Claims	1 - 7, 12, 14, 16
	No:	Claims	8 - 11, 13, 15, 17
Inventive step (IS)	Yes:	Claims	1 - 7, 12, 14, 16
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1 - 17
	No:	Claims	

**2. Citations and explanations**

**see separate sheet**

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

**see separate sheet**

**Ad IV.:**

- 1.1 The present application does not fulfill the requirements of Rule 13 PCT. An international application shall relate to one invention only or to a group of inventions so linked as to form a single general inventive concept. The requirement of unity shall be fulfilled only when there is a technical relationship among those inventions involving one or more of the same or corresponding special technical features (STF). The expression STF shall mean those technical features that define a contribution which each of the claimed inventions considered as a whole, makes over the prior art (Rule 13.1 and 13.2 PCT).
- 1.2 The separate groups of inventions are:  
**A** Claims 1 - 7  
**B** Claims 8 - 17
- 1.3 The groups are not so linked as to form a single general inventive concept for the following reasons:  
The independent claims 1 and 8 present solutions to different technical problems. Claims 1 - 7 are directed to a process for the production of a frozen food product comprising AFP and which submitted to a compaction step.  
Claim 8 - 17 relate to a frozen free-flowing particulate food product comprising AFP and processes for the production thereof.
- The technical feature in common between groups **A** and **B** is a frozen food product comprising AFP.
- This feature is not new with regard to D1, D2 and D3 (see point V.). Thus, no technical relationship involving more of the same corresponding special features exists among the above listed groups of invention.
- 1.4 According to Rule 68.1 PCT, the International Preliminary Examining Authority proceeds with the International Preliminary Examination in respect of the entire international application.

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/EP98/08552

**Ad V.:**

1. Reference is made to the following documents:

D1: US-A-5 676 985

D2: US-A-5 620 732, cited in the application

D3: WO-A-90/13571, cited in the application, not cited in the international search report.

D5: EP-A-0 561 118 cited in the application

1.1 The prior art documents D1 and D2 disclose the production of ice cream comprising AFPs. Superior freeze properties are achieved. D1 points to the use of any suitable conventional freezer operation (col. 6, l. 18 - 23). The same applies for D2 (examples 1 and 2). The method of D2 does not require a hardening step prior to storage. Both documents stress the importance to control the crystal size in order to obtain the desired mouthfeel (D1, col. 1, l. 26 - 50; D2, col. 1, l. 32 - 50; col. 4, l. 54 - 60)

1.2 D3 disclose antifreeze polypeptides. D3, p. 25, l. 1 - 15 and examples 3A - 3C relate to a crystal growth assay. This "splat" assay consists in the instant surface freezing (-75°C) of a solution comprising of AFPs. The frozen products have very minute ice crystals of the required size (see example I of the present application). The splats are scraped from the cold surface and transferred to the cryostage. The frozen splats are edible and are therefore regarded as frozen food/confectionary products.

1.3 D5 is directed to screw extruders for the production of frozen food products such as ice cream. The relation between this production method and the resulting very small crystal size is disclosed (col. 10, l. 10 - 26; col. 7, l. 25 - drawings, claim 1).

2. Claims 1 - 7 (Group A)

2.1 The requirements of Article 33(2) PCT are met for the subject-matter of claims 1 - 7. The prior art does not disclose a process for the production of a frozen food product comprising AFP wherein the process comprises a compaction step (see D1 - D3).



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/EP98/08552

2.2 The problem solved with the additional compaction step is the have desirably small ice crystals which are not aggregating. A more favourable texture is achieved. There are no incentives given in D1 or D2 to further improve the texture of the given products. Therefore no hint can be seen for the skilled worker to combine the methods of D1 or D2 with a method of D5. The requirements of Article 33(3) PCT seem therefore to be met.

3. Claims 8 - 17 (Group B)

3.1 The subject-matter of claims 8, 9, 10, 11, 13, 15 and 17 does not meet the requirements of Article 33(2) PCT with respect to D3, especially example 3B. According to the description of the present application, a particulates with the desired free flow characteristics comprise flakes, frozen droplets, frozen powders, pellets, rods and snow wherein the product has been rapidly frozen (p. 11, l. 28 - p. 12, l. 4; example II). Since the surface scraped splats of the splat test of D3 provide all the technical features of the cited claims, they are regarded as novelty destroying for the subject-matter claimed therein. The same applies for the processes according to claims 15 and 17.

3.2 The subject-matter of claims 12, 14 and 16 is not disclosed in the prior art. The requirements of Article 33(2) PCT would therefore be met. There are also no hints for the skilled person in view of the prior art to provide a particulate frozen food product with reduced tendency of the particulates to aggregate with the technical features as comprised in claims 12, 14 and 16. The requirements of Article 33(3) PCT would therefore be met.

4. The subject-matter of claims 1 - 17 meets the requirements of Article 33(4) PCT.

**Ad VIII.:**

1. The subject-matter of claims 15 and 17 is redundant (Article 6 PCT).

Claims

1. A process for the manufacture of a frozen food product comprising anti-freeze peptides, wherein the process  
5 comprises;
- (i) an optional rapid freezing step such that the product reaches a temperature of  $-5^{\circ}\text{C}$  or lower within 30 seconds;  
and  
10
- (ii) a compaction step using a screw extruder or a compactor.
2. A process according to claim 1 wherein in step (i) the  
15 product is frozen to a temperature of  $-5^{\circ}\text{C}$  or lower in from 0.01 to 25 seconds.
3. A process according to claim 1 wherein in step (i) the  
20 product is frozen to a temperature of  $-5^{\circ}\text{C}$  or lower in from 1 to 15 seconds.
4. A process according to any preceding claim, wherein  
step (i) involves one or more of;
- 25 (a) surface freezing, preferably film freezing, onto a cold surface;
- (b) freezing of a supercooled system;
- (c) decompression freezing;
- (d) freezing at very low temperatures;
- 30 (e) rapid particulate freezing, preferably condensation freezing.
5. A process according to any preceding claim, wherein  
step (i) involves drum freezing of the product.

AMENDED SHEET

*do not enter per attorney's request*

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6. A process according to claim 1, wherein in step (ii) a screw extruder is used.

5 7. A process according to claim 1, wherein in step (ii) the extrusion temperature of the frozen food product is less than -8 °C.

10 8. A free-flowing, particulate food product comprising anti-freeze peptide, which maintains its free-flowing nature during storage, obtainable by rapidly freezing the food product such that the food product reaches a temperature of -5°C or lower within 30 seconds.

15 9. A free-flowing, particulate food product according to claim 8, wherein the food product is rapidly frozen such that the food product reaches a temperature of -5°C or lower in from 0.01 to 25 seconds.

20 10. A free-flowing, particulate food product according to claim 8, wherein the food product is rapidly frozen such that the food product reaches a temperature of -5°C or lower in from 1 to 15 seconds.

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11. A free-flowing, particulate food product according to claim 8, wherein the food product is rapidly frozen using one or more of;

- (a) surface freezing, preferably film freezing, onto a cold surface;
- (b) freezing of a supercooled system;
- (c) decompression freezing;
- (d) freezing at very low temperatures;
- (e) rapid particulate freezing, preferably condensation freezing.

12. A free-flowing, particulate food product according to claim 8, wherein the food product is rapidly frozen by drum freezing.

13. A free-flowing, particulate food product according to claim 8, wherein the food product is a frozen confectionery product.

14. A free-flowing, particulate food product according to claim 8, wherein the anti-freeze peptide is AFP Type III HPLC 12.

15. A process to provide a free-flowing, particulate food product comprising rapidly freezing the food product such that the food product reaches a temperature of -5°C or lower within 30 seconds.

16. A process to provide a free-flowing, particulate food product, wherein the food product is rapidly frozen by drum freezing.

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17. Use of a process comprising rapidly freezing a food product such that the food product reaches a temperature of  $-5^{\circ}\text{C}$  or lower within 30 seconds to provide a free-flowing, particulate food product.

5

AMENDED SHEET

# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>F 7414 (V)</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/EP 98/ 08552</b>	International filing date (day/month/year) <b>23/12/1998</b>	(Earliest) Priority Date (day/month/year) <b>22/01/1998</b>
Applicant  <b>UNILEVER N.V. et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

**1. Basis of the report**

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☐ None of the figures.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 98/08552

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 A23G9/02

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A23G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 676 985 A (WU YALING ET AL) 14 October 1997	7-10
A	see column 6, line 18-23; claim 1 ---	1-6
A	US 5 620 732 A (CLEMMINGS JOHN F ET AL) 15 April 1997 cited in the application see claims 1-4; examples 1,2 ---	1-14
P, A	WO 98 04699 A (UNILEVER PLC ; UNILEVER NV (NL)) 5 February 1998 cited in the application see examples 3,4 --- -/--	1-14



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## ° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&amp;" document member of the same patent family

Date of the actual completion of the international search

9 June 1999

Date of mailing of the international search report

29/06/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2

NL - 2280 HV Rijswijk

Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,

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Authorized officer

De Jong, E

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 98/08552

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 561 118 A (MILCHHOF EISKREM GMBH & CO KG ;DEUTSCHES INST LEBENSMITTELTEC (DE)) 22 September 1993 cited in the application see claim 1 . -----	7-14



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 98/08552

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5676985	A	14-10-1997	AT 179868 T	15-05-1999
			AU 3602395 A	06-05-1996
			CA 2202373 A	25-04-1996
			WO 9611586 A	25-04-1996
			EP 0785727 A	30-07-1997
			JP 10509304 T	14-09-1998
US 5620732	A	15-04-1997	AU 704570 B	29-04-1999
			AU 5790496 A	30-12-1996
			CA 2195950 A	19-12-1996
			EP 0783254 A	16-07-1997
			JP 10508759 T	02-09-1998
			WO 9639878 A	19-12-1996
WO 9804699	A	05-02-1998	AU 3443797 A	20-02-1998
			AU 3621297 A	20-02-1998
			AU 3621397 A	20-02-1998
			AU 3693497 A	20-02-1998
			DE 19732135 A	26-02-1998
			DE 19732136 A	29-01-1998
			WO 9804146 A	05-02-1998
			WO 9804147 A	05-02-1998
			WO 9804148 A	05-02-1998
			EP 0918863 A	02-06-1999
			FR 2751657 A	30-01-1998
			FR 2751513 A	30-01-1998
			GB 2315752 A	11-02-1998
			GB 2315753 A	11-02-1998
			IT MI971752 A	25-01-1999
			IT MI971755 A	25-01-1999
EP 0561118	A	22-09-1993	DE 4202231 C	09-06-1993
			US 5345781 A	13-09-1994
			AT 158151 T	15-10-1997
			DK 561118 T	05-01-1993

## PATENT COOPERATION TREATY

RECEIVED 30 JUN 1999

PCT

From the INTERNATIONAL SEARCHING AUTHORITY

RECEIVED  
PATENT DEPARTMENT

2 JUL 1999

COLWORTH

NOTIFICATION OF TRANSMITTAL OF  
THE INTERNATIONAL SEARCH REPORT  
OR THE DECLARATION

To:  
UNILEVER N.V.  
Patent Department  
Attn. Joppe, Hermina C.P.  
P.O. Box 137  
NL-3130 AC Vlaardingen  
NETHERLANDS

PATALE TERMIN

(PCT Rule 44.1)

Voorle open

Parceel

Date of mailing  
(day/month/year)

29/06/1999

Applicant's or agent's file reference

F 7414 (V)

FOR FURTHER ACTION

See paragraphs 1 and 4 below

International application No.

PCT/EP 98/08552

International filing date  
(day/month/year)

23/12/1998

Applicant

UNILEVER N.V. et al.

1. ☒ The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

**Filing of amendments and statement under Article 19:**

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

**When?** The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

**Where?** Directly to the International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland  
Fascimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ With regard to the protest against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Further action(s):** The applicant is reminded of the following:

Shortly after 18 months from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

Within 19 months from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within 20 months from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority



European Patent Office, P.B. 5818 Patentlaan 2  
NL-2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.  
Fax: (+31-70) 340-3016

Authorized officer

Cristina Iacoponi

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

## INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

### What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

### When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

### Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

### How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

### What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:  
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:  
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:  
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or  
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:  
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

**"Statement under article 19(1)" (Rule 46.4)**

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

**Consequence if a demand for international preliminary examination has already been filed**

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

**Consequence with regard to translation of the international application for entry into the national phase**

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

# PATENT COOPERATION TREATY

# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>F 7414 (V)</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/EP 98/ 08552</b>	International filing date (day/month/year) <b>23/12/1998</b>	(Earliest) Priority Date (day/month/year) <b>22/01/1998</b>
Applicant  <b>UNILEVER N.V. et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.



It is also accompanied by a copy of each prior art document cited in this report.

**1. Basis of the report**

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.



the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing:



contained in the international application in written form.



filed together with the international application in computer readable form.



furnished subsequently to this Authority in written form.



furnished subsequently to this Authority in computer readable form.



the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.



the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐

**Certain claims were found unsearchable** (See Box I).

3. ☐

**Unity of invention is lacking** (see Box II).

4. With regard to the **title**,



the text is approved as submitted by the applicant.



the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,



the text is approved as submitted by the applicant.



the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.



as suggested by the applicant.



because the applicant failed to suggest a figure.



because this figure better characterizes the invention.



None of the figures.

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 A23G9/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A23G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 676 985 A (WU YALING ET AL) 14 October 1997	7-10
A	see column 6, line 18-23; claim 1 ---	1-6
A	US 5 620 732 A (CLEMMINGS JOHN F ET AL) 15 April 1997 cited in the application see claims 1-4; examples 1,2 ---	1-14
P,A	WO 98 04699 A (UNILEVER PLC ;UNILEVER NV (NL)) 5 February 1998 cited in the application see examples 3,4 ---	1-14
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

9 June 1999

Date of mailing of the international search report

29/06/1999

Name and mailing address of the ISA

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Authorized officer

De Jong, E

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 561 118 A (MILCHHOF EISKREM GMBH & CO KG ;DEUTSCHES INST LEBENSMITTELTEC (DE)) 22 September 1993 cited in the application see claim 1 -----	7-14

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 98/08552

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